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Coplen, Tyler B.; Brand, Willi A.; Gehre, Matthias; Groning, Manfred; Meijer, Harro A. J.; Toman, Blaza; Verkouteren, R. Michael; Gröning, Manfred; Coplen, B.T.; Gehre, [No Value]

Published in:
Rapid Communications in Mass Spectrometry

DOI:
10.1002/rcm.2727

RAPID COMMUNICATIONS IN MASS SPECTROMETRY
Rapid Commun. Mass Spectrom. 2006; **20**: 3165–3166
Published online in Wiley InterScience (www.interscience.wiley.com) DOI: 10.1002/rcm.2727

RCM

Guest Editorial

After two decades a second anchor for the VPDB δ^{13}C scale†

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In 1985, the primary recommendation of a Consultants' Group Meeting of the International Atomic Energy Agency (IAEA)[1] was that a new (Vienna Peedee Belemnite) VPDB δ^{13}C scale be established with NBS 19 carbonate assigned to be +1.95‰ as its single anchor. This recommendation improved δ^{13}C measurement uncertainties,[2] especially those of materials with δ^{13}C values near 0‰. A fundamental problem remained that materials with δ^{13}C values far from 0‰, such as NBS 22 oil, had much poorer uncertainties.[2,3] Recognizing that two-point calibrations of the δ^{2}H and δ^{18}O scales substantially improved the agreement among laboratories,[4] the IAEA convened a panel in 2004 to review stable carbon isotopic reference materials and to recommend a second reference material for two-point normalization of the δ^{13}C scale.

Four laboratories (Centrum voor Isotopen Onderzoek, Groningen, The Netherlands; Max-Planck-Institute for Biogeochemistry, Jena, Germany; UFZ Leipzig-Halle, Leipzig, Germany; US Geological Survey, Reston, VA, USA) performed analytical measurements. Participants at the US National Institute of Science and Technology (NIST) headed the task to estimate consensus means and uncertainties using multivariate Bayesian techniques. Collectively, the laboratories performed 1055 state-of-the-art continuous-flow elemental-analyzer mass spectrometry measurements using the general method of Qi *et al*.[5] on selected organic and inorganic carbon isotopic reference materials. Aims of the work included determining consensus δ^{13}C values of stable carbon isotopic reference materials and confirming that isotopic materials measured in this study are isotopically homogeneous in amounts used in continuous-flow methods [m(C) of approximately ~40 µg]. Based on high precision mass spectrometric measurements,[6,7] a consensus value of −46.6‰ was assigned to L-SVEC lithium carbonate.[8] The results (Table 1) were provided to the International Union of Pure and Applied Chemistry (IUPAC).

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RECOMMENDATIONS

Following recommendations of the Commission on Isotopic Abundances and Atomic Weights in August 2005 at the 43rd

Table 1. Reference δ^{13}C values of stable carbon isotopic reference materials[a,b,c]

Name	Description	$\delta^{13}C \times 10^3$
USGS41	L-glutamic acid	+37.63
IAEA-CO-1	calcium carbonate	+2.49
NBS 19	calcium carbonate	+1.95
RM 8562	carbon dioxide	−3.72
NBS 18	calcium carbonate	−5.01
IAEA-CO-8	calcium carbonate	−5.76
IAEA-CH-6	sucrose	−10.45
RM 8564	carbon dioxide	−10.45
USGS24	graphite	−16.05
IAEA-CH-3	cellulose	−24.72
USGS40	L-glutamic acid	−26.39
IAEA-600	caffeine	−27.77
IAEA-601	benzoic acid	−28.81
IAEA-602	benzoic acid	−28.85
NBS 22	oil	−30.03
IAEA-CH-7	polyethylene	−32.15
RM 8563	carbon dioxide	−41.59
L-SVEC	lithium carbonate	−46.6
IAEA-CO-9	barium carbonate	−47.32

[a] Recommendations from a Consultants' Meeting of the IAEA.
[b] δ^{13}C values expressed relative to VPDB (δ^{13}C of NBS 19 ≡ +1.95‰) and normalized to δ^{13}C of L-SVEC ≡ −46.6‰.
[c] Uncertainties and other data can be downloaded from the internet.[10]

Published in 2006 by John Wiley & Sons, Ltd.

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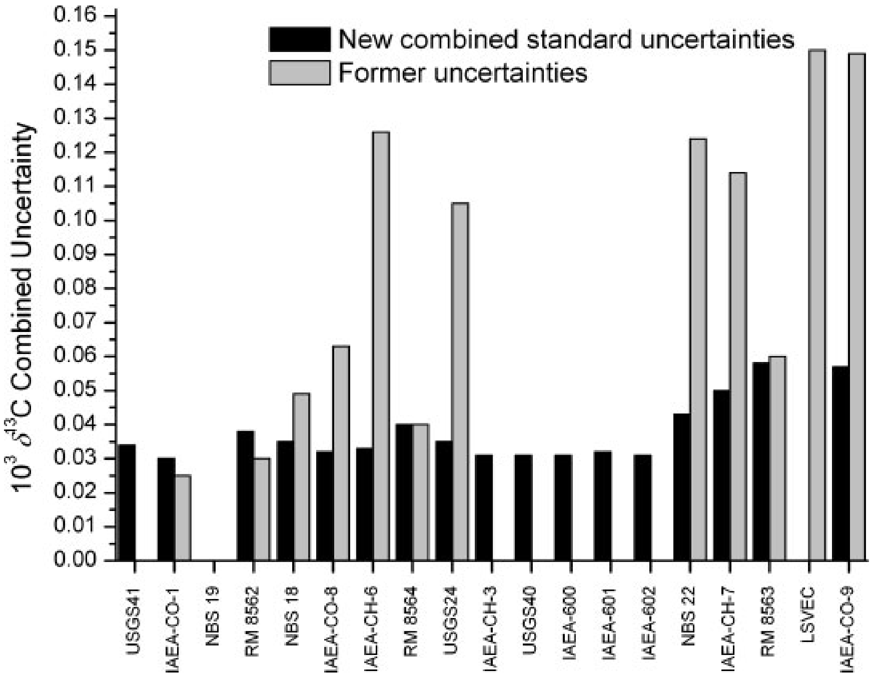

Figure 1. Improvement in new combined standard uncertainties (1-σ) for δ^{13}C reference materials compared with previously assessed uncertainties (1-σ). By consensus, NBS 19 has no associated uncertainty on either the former normalized scale or the new normalized scale, and L-SVEC has no associated uncertainty on the new normalized scale.

General Assembly of IUPAC in Beijing, and recommendations of an IAEA panel:[8]

1. δ^{13}C values of all carbon-bearing materials should be measured and expressed relative to VPDB on a scale normalized by assigning consensus values of −46.6‰ to L-SVEC lithium carbonate and +1.95‰ to NBS 19 calcium carbonate.
2. Authors should clearly state so in their reports.
3. Authors are encouraged to report their measurement results for δ^{13}C values of NBS 22 oil, USGS41 L-glutamic acid, IAEA-CH-6 sucrose, or other internationally distributed reference materials, as appropriate for the measurement method.

DISCUSSION

The average variations (standard deviations) in results across laboratories were lowered 39% to 47% (Fig. 1). The δ^{13}C values of some materials are striking different. The δ^{13}C value of NBS 22 is −30.03‰, which is substantially more negative than the value reported by Gonfiantini *et al.*[9] of −29.74‰, but it is in line with the value of Qi *et al.*[5] of −29.99‰ (normalized to an L-SVEC value of −46.6‰) and is in accord with the observation by Stalker *et al.*[3] that δ^{13}C values of NBS 22 and other organic reference materials are too positive.

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DOI: 10.1002/rcm